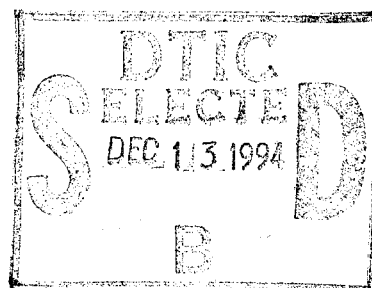


TITLE: LARGE AREA SMART PIEZOELECTRIC AND PYROELECTRIC SENSORS

**Contract: DAJA 45-93-C-0017
(R & D 6980-EE-01)**



SIXTH INTERIM REPORT

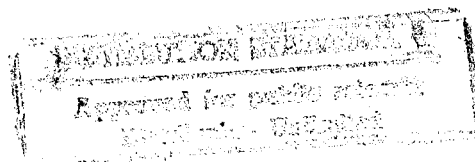
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November, 1994



The nature of the pyroelectric properties of the composite PTCa/Epikote 828 with 50/50 and 60/40 vol% was reported in the fifth interim report.

The present report provides an account of the preparation of pure lead titanate (PT) and calcium modified lead titanate (PTCa) by the Sol-Gel process. X-ray Spectroscopic Structural Analysis and Differential Scanning Calorimetric (DSC) studies of the ceramic grains produced by this technique were made and the results are given in this report.

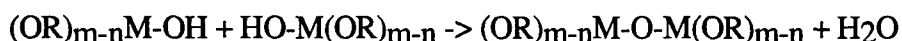
The sol-gel method for preparation of ferroelectric ceramics can offer many advantages over conventional processing techniques. Ceramics produced via the sol-gel method show high degrees of purity and homogeneity, can produce fine powders as well as being able to be formed into a variety of structures and they possess the ability to be processed at lower temperatures.

Sol-gel processing (1) is the name given to the production of a gel from a solution of precursors. Precursors, usually metal alkoxides, undergo a reaction with water, called *hydrolysis* where the hydroxyl ion becomes attached to the metal atom as in the following reaction:

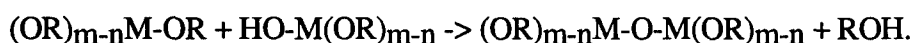


Where M is a metal and R represents a proton or other ligand. If there is enough water this process of hydrolysis can go to completion (so that all the OR groups are replaced by OH), or stop while the metal is only partially hydrolysed, $M(OR)_{m-n}(OH)_n$.

Two partially hydrolysed molecules can link together in a *condensation* reaction, such as



or



This type of reaction can continue to build larger and larger metal containing molecules by the process of *polymerisation*. The number of bonds the monomer can form is called its

per
form so

functionality, f . If $f > 2$ then the polymer chains can be joined by crosslinks to form a three-dimensional structure. If the size of the polymer molecule reaches macroscopic dimensions so that it extends throughout the solution, the substance is said to be a gel. Thus a gel is a substance that contains a continuous solid skeleton enclosing a continuous liquid phase. Gels can also be formed from particulate sols where the particles are held together by van de Waals forces.

Once the gel has been obtained from a solution, i.e. after the process of hydrolysis and condensation, the gel must be *aged*. Ageing is the term given to the process of change in structure and properties after gelation which may involve further condensation, dissolution and reprecipitation of monomers or oligomers, or phase transformations within the solid or liquid phases. Shrinkage of the gel occurs either due to a process called *syneresis*, contraction of the network due to bond formation or attraction between particles, or as liquid evaporates during drying, both causing deformation of the network and transport of liquid through the pores. Drying at room temperature results in a *xerogel* which often is reduced in volume by a factor of 5 to 10 compared to the original wet gel. Most xerogels are *amorphous* but many crystallise upon heating which is the object of producing ferroelectric ceramics via the sol-gel method.

The thermal processing of a gel to produce the required ceramic needs to be undertaken in various stages (2). Initial drying at an elevated temperature is required to remove the remaining solvent used in the preparation of the gel. This is normally performed at around 100°C for most solvents. The dried gel is then consolidated at a higher temperature, usually no more than 300°C, to remove most of the other organics present, then fired at higher temperatures, usually greater than 500°C, to produce the final crystallised ceramic powder.

3. Preparation

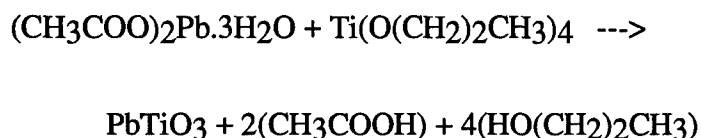
Pure lead titanate, (PT), was prepared using starting materials for the reaction of lead (II) acetate trihydrate, $[(CH_3COO)_2Pb \cdot 3H_2O]$ and titanium (IV) propoxide, $[Ti(O(CH_2)_2CH_3)_4]$. The materials were weighed to provide a 1:1 molar ratio of lead to titanium. Weights being calculated from 'Molar weight = Formulae weight / Purity of substance'. The solvent used was propanediol-(1,3), $[HO(CH_2)_3OH]$. The materials were dissolved separately in solvent and then combined in the reaction flask. This mixture was then allowed to reflux at 100°C overnight. A thick clear viscous gel was formed after a number of hours which was reduced by rotary evaporation for about four hours. This gel was poured into flat dishes and allowed to dry for about a week. Water for hydrolysis came from the water contained within the lead (II) acetate trihydrate. After about a week the gel had formed monoliths which showed signs of shrinkage. Further drying and shrinkage was observed if the gel was left for longer periods of time.

Drying of the gel in an oven was performed in a number of stages. The initial drying was performed at temperatures no greater than 100°C for about three hours. This enabled the removal of any remaining water. The temperature of the oven was increased slowly up to 300°C in steps of 25° and kept at these temperatures for an hour each. This enabled the gel to dry out and release the remaining solvents and other organics present without reaction. Above 300°C the temperature could be increased at a higher rate up to the sintering temperature of 900-1000°C.

Lead titanate modified by replacing some of the Pb^{2+} ions with Ca^{2+} was also attempted using exactly the same method as described above. Attempts were made to produce $\text{Pb}_{1-x}\text{Ca}_x\text{TiO}_3$ with an x value of 0.24 using calcium acetate hydrate, $[(\text{CH}_3\text{COO})_2\text{Ca} \cdot n\text{H}_2\text{O}]$. The constituent materials were dissolved separately in solvent. The Ca^{2+} and Pb^{2+} ions being mixed together prior to the addition of the Ti^{4+} ions. After refluxing a pale opaque gel was formed which when allowed to dry in flat dishes produced monoliths showing signs of shrinkage.

4. Results and Discussion

The overall reaction taking place to produce pure lead titanate is



This reaction takes place through a series of hydrolysis and condensation reactions such as described earlier.

The resulting powders produced after firing at various temperatures and the initial gel were analysed using a variety of techniques namely X-Ray Diffraction, Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA) and Derivative Thermogravimetry (DTG) (3).

X-Ray Diffraction Method:- The powder camera method of X-ray diffraction was performed on pellets formed from the powders to investigate the crystal structure. This method gave the crystallinity of the samples and the crystal lattice ratios of the tetragonal structure.

Differential Scanning Calorimetry (DSC):- This method of analysis involves the measurement of the heat flow into or out of the sample, compared to a known reference, in an attempt to keep a zero temperature difference between sample and reference as the environment is heated at a constant rate.

Differential Thermal Analysis (DTA):- This method involves the measurement of the temperature of a sample compared with the temperature of a thermally inert reference material as a function of temperature as the sample and reference are heated at a constant rate. Temperature changes in the sample are due to exothermic or endothermic reactions.

Derivative Thermogravimetry (DTG):- In this technique the weight of the sample is recorded as a function of temperature or time as the sample is heated at a constant rate. Weight loss will then be due to evaporation or sublimation of the sample.

The gels of PT dried at room temperature were found to be amorphous by X-ray diffraction as shown in fig. 1. Crystallisation occurred at about 250-300°C, this is evident from the X-ray diffraction spectrums, fig. 2, and from the DTA and DSC output, both of which show a sharp exothermic reaction occurring around these temperatures. From X-ray spectrum taken of samples heated to temperatures of 600°C and 800°C a high degree of crystallinity can be observed reflecting a tetragonal crystal structure with a tetragonality (c/a lattice ratio) of 1.066, fig 3. This figure agrees well with figures quoted in literature (4).

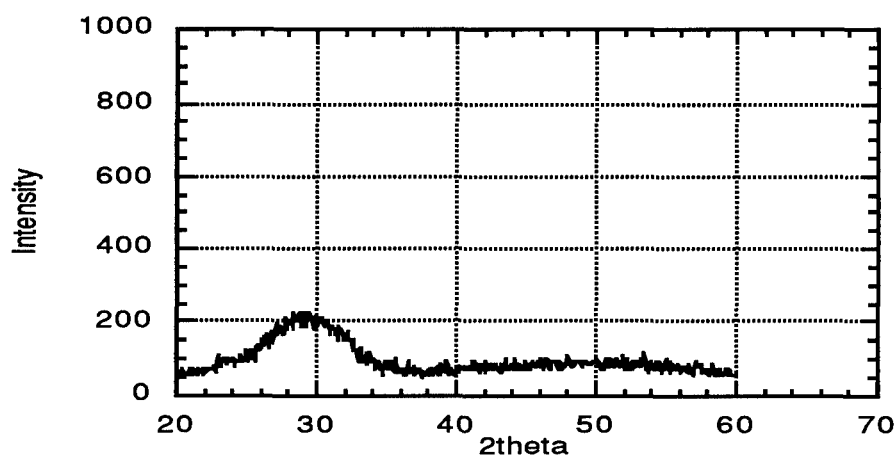


Fig. 1: X-ray diffraction of PT gel dried at room temperature.

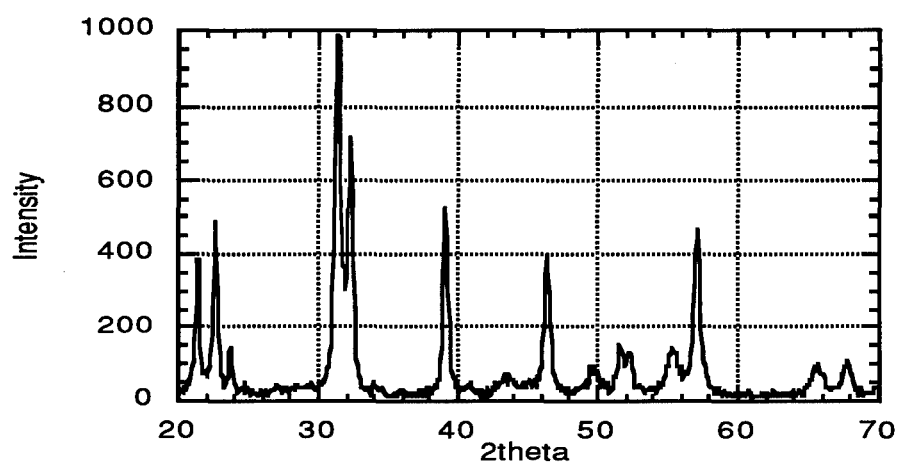


Fig. 2: Crystallisation of PT occurring at 250-300°C

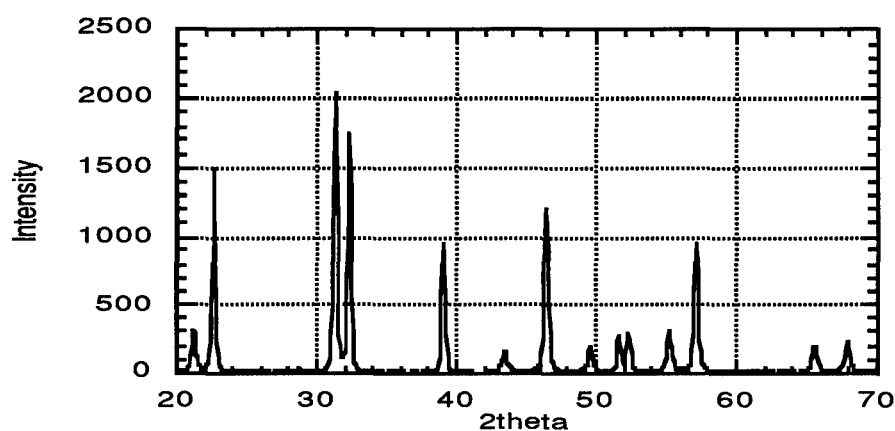


Fig. 3: X-ray spectrum of PT heated to 800°C showing high degree of crystallinity.

The transitional temperature of tetragonal to cubic (Curie temperature) was observed, by sharp endothermic (upon heating) response during DTA and DSC runs, fig. 4, to be 487°C, which is also in good agreement with values quoted for lead titanate (4, 5).

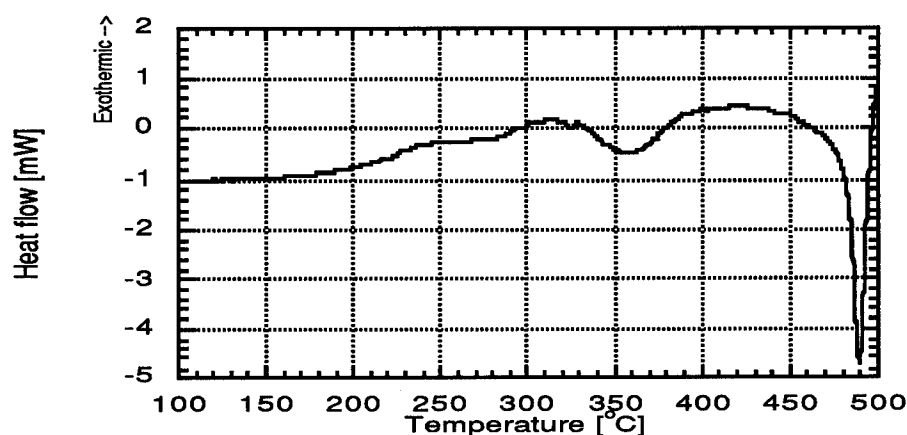
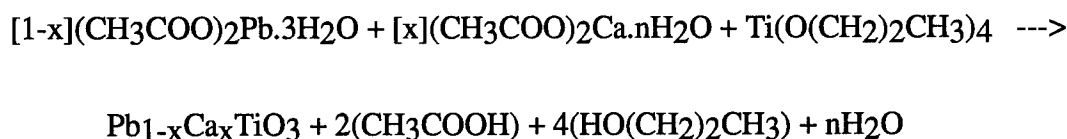


Fig. 4: DSC response showing the Curie temperature of PT

The overall reaction taking place to produce calcium modified lead titanate is



Again this reaction takes place by a series of hydrolysis and condensation reactions.

The gel and the crystalline powders produced of calcium modified lead titanate (PTCa) were analysed using the same methods as described before. The gel appeared to be amorphous until heated to temperatures of around 450 - 500°C, above which it crystallised into a tetragonal crystal structure with c/a ratio of 1.058 as shown in fig 5. DSC measurements on the crystalline powders showed an endothermic response at around 412°C, which is believed to be the ferroelectric phase transition, fig 6. DTA measurements on the powders failed to detect the Curie temperature of PTCa due to the fact the response was small.

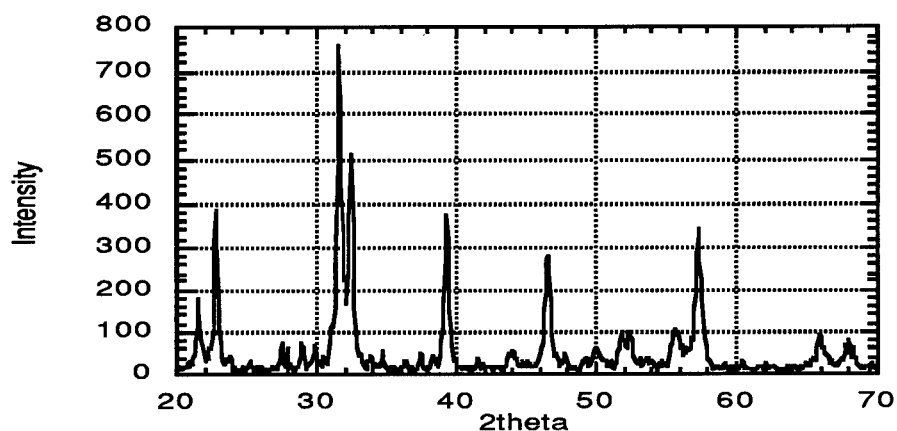


Fig. 5: X-ray spectrum of PTCa powder after heated to 800°C

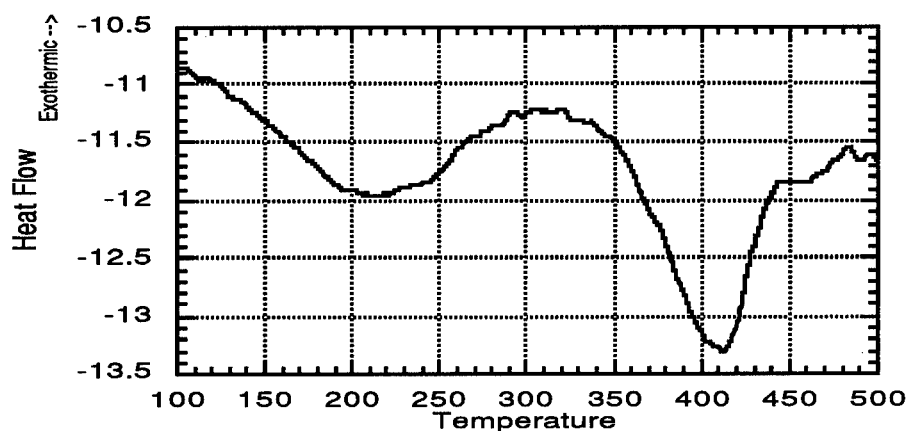
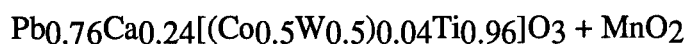


Fig. 6: DSC response of PTCa heated to 500°C

In this study commercially produced PTCa, produced by conventional methods, with chemical formulae



was also analysed for comparison purposes. Measured values of this ceramic produce a c/a ratio of 1.039 and Curie temperature of 260°C.

The substitution of isovalent ions causes the Curie temperature to be shifted, usually downwards. The amount of shift will reflect the percentage of isovalent substitutions. Similarly the c/a ratio will also be shifted accordingly (6). The values of the Curie temperature and c/a ratio of the PTCa produced via sol-gel method differ from those found from the commercially produced ceramics. These variations in values are due to the differing isovalent and non-

isovalent substitutions of the two ceramics. The measured c/a ratio, for the sol-gel derived PTCa, of 1.058 corresponds well with results from other researchers working with the $\text{Pb}_{0.76}\text{Ca}_{0.24}\text{TiO}_3$ system. Ichinose et al (5) reports a c/a ratio of 1.057. The observed Curie temperature is believed to be of about the right value but we have found no data to confirm this as yet.

Investigations of the sol-gel derived PTCa using Energy Dispersive X-Ray (EDX) analysis techniques show the average calcium content to be in good agreement with that of the commercially produced ceramic. The sol-gel derived ceramic however does appear to have a wider spread of calcium content with respect to each grain. This might explain the broadening of the DSC peak corresponding to the ferroelectric transition. The reason behind the apparent spread of x values from grain to grain within the ceramic is not fully understood yet, but may be due to a mismatch of hydrolysis and condensation rates of the A site metals.

5. Effect of Solvent

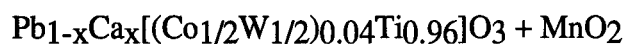
During this study various solvents were used to prepare the ceramic precursor gels. Propanediol - (1,3) has been mentioned earlier. Other solvents used were propanediol - (1,2), methoxyethanol and acetic acid which produced gels from the precursors. 2-Butanol and N-N-Dimethylformamide were also used and these solvents tended to produce precipitation which upon drying produced the required ceramic.

PTCa produced using 2-butanol or N-N-demethylformamide formed via a precipitated powder had varying Curie temperatures and tetragonality of 421°C, 1.0181 (for 2-butanol) and 470°C, 1.0566 (for N-N-dimethylformamide).

It was found that the solvents used which produced a monolithic gel rather than a precipitated gel produced results which were more consistent and in accordance with other workers. This could be explained from the point of view of differing hydrolysis, condensation and precipitation rates as stated earlier.

6. Further Work

The method used here in this work to produce PTCa has been expanded from a successful method previously used to produce PT from metal alkoxide precursors (7). Other workers have produced PTCa via the sol-gel route using differing methods such as coprecipitation (8) (9) or gel precipitation (10). Further work would involve the sol-gel synthesis of PTCa with the chemical formulae



by the addition of dopants in the processing method to produce a ferroelectric ceramic of high anisotropy, with respect to its planar and thickness coupling factors, produced with high purity and homogeneity. The ability to produce ceramics of fine grain and size consistency will allow the fabrication of very thin composite films.

7. References

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